AD NUMBER

AD854108

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; JUN 1969. Other requests shall be referred to Air Force Materials Lab., Attn: MAAM, Wright-Patterson AFB, OH 45433.

AUTHORITY

Air Force Materials Lab ltr dtd 2 Mar 1972

DMIC review OF RECENT DEVELOPMENTS

Corrosion and Compatibility

JUN 25

W. E. Berry • June 4, 1969

AD854108

GENERAL

A literature survey on the corrosion and compatibility of materials with rocket fuels and oxidizers has been prepared ~~by TRW Systems~~ in connection with the use of valves in a spacecraft liquid propulsion system.(1) In addition to corrosion and compatibility, the survey also contains information on shock sensitivity, lubricity, viscosity, radiation tolerances, effects of leakage, and other properties of propellants. Fuels and oxidizers covered include: hydrazine, monomethyl hydrazine, unsymmetrical dimethylhydrazine, aerozine-50, pentaborane, diborane, Hybaline A-5, liquid petroleum gases, liquid hydrogen, gelled propellants, nitrogen tetroxide, liquid oxygen, liquid fluorine, chlorine trifluoride, chlorine pentafluoride, oxygen difluoride, perchloryl fluoride, liquid oxygen-liquid fluorine (FLOX), nitrogen trifluoride, nitryl fluoride, and tetrafluorohydrazine.

ALUMINUM ALLOYS

The design and processing trade-offs to circumvent the stress-corrosion cracking problem with 7079-T6 aluminum in aircraft structural forgings has been discussed by Northrop Norair.(2) These trade-offs included: (1) change in forging designs to improve grain flow or to incorporate compressive stress relieving (-T652), (2) change in material or heat treatment such as 7075-T73, 7175-T736, or 7001-T75, (3) controlled shot peening to introduce compressive stresses, and (4) control of all machining and processing sequences in manufacture from rough machining in the T-411 condition through final shot peening and anodizing.

IRON-BASE ALLOYS

Steels

A method of protecting metal fasteners from corrosion in tropical marine environments has been developed at the Pacific Missile Range.(3) It consists of pressing a polyethylene sealing cap containing a thermoplastic, synthetic rubber-polysulfide base sealant over the end of the exposed fastener. The results of salt-spray tests and a 16-month weathering test at Kwajalein Atoll revealed little attack on 18Cr-8Ni steel, medium-carbon steel, and cadmium-plated bolts used to fasten aluminum-to-aluminum, steel-to-aluminum, magnesium-to-magnesium, and steel-to-steel.

A new environmental cause of stress-corrosion cracking of mild- and low-alloy steels has been described by the Japanese.(4) Transgranular cracking occurred in U-bend specimens within 1 week's exposure to water at 104 F in an autoclave that was pressurized with 35 psia carbon dioxide and 178 psia carbon monoxide.

The effect of chemical composition on the stress-corrosion cracking behavior of precracked HY-150 steel in 3 percent sodium chloride solution has been studied by U. S. Steel.(5) All steels investigated failed by stress-corrosion cracking, but the stress-corrosion cracking susceptibility (K_{ISCC}) was affected by chemical composition of the steel. The K_{ISCC} was correlated with toughness, but was independent of yield strength. The chemical composition had a strong effect on toughness which, because of the strong relationship, affected the K_{ISCC}. Optimum composition for a light-gage (<2-in.-thick) HY-150 steel that would provide maximum resistance to stress-corrosion cracking, maximum toughness, and high resistance to weld cracking was 6.5Ni-0.4Cr-0.7Mo-0.06 to 0.08V.

Crack extension in fatigue-cracked notched-bend specimens of high-strength steels in 3.5 percent NaCl solution has been studied by Boeing.(6) The 300M, H-11, Maraging 250, and 9Ni-4Co-0.45C (martensitic) steels failed along a single crack extending along the fatigue crack plane. The 4430V, 9Ni-4Co-0.30C, and 9Ni-4Co-0.45C (bainite) steels exhibited either a single crack extension or two divergent cracks extending at an angle from the tip of the fatigue crack -- depending upon the initial stress intensity level K_{Ii}. The divergent cracks extended preferentially along the regions of stress relaxation.

Stainless Steels

The crevice corrosion of stainless steels in quiescent seawater is being investigated at the Naval Research Laboratory.(7) Stainless steels studied were Types 205, 304, 316, 410, and 430, 17-4PH H1025, 21Cr-6Ni-9Mn, and 20CB-3. All exhibited severe crevice corrosion except the 20CB-3 alloy which exhibited only a moderate amount of attack. Steel anodes mitigated crevice attack in all the stainless steels, but did not prevent random pitting on fully exposed surfaces. Aluminum anodes prevented both crevice attack and random pitting, but caused accelerated cracking of the 17-4PH H1025 alloy.

The stress-corrosion cracking behavior of vacuum-melted Armco PH13-8Mo in the H1000 condition has been reported by McDonnell.[8] Bent beam specimens stressed to 90 and 95 percent of the room-temperature yield strength of 200,000 psi were alternately immersed 10 minutes in synthetic seawater and dried in air for 50 minutes. No cracking was observed in six replicate specimens at each stress level after 84 days' exposure. Specimens of Armco 17-4PH H900 cracked in this same test.

NICKEL ALLOYS

An analytical study has been made by NASA Lewis of the flow reduction characteristics due to the oxidation of wire-form porous sheets of N155, Driver-Harris 242, TD Nickel-Chromium, and Hastelloy X.[9] Pore size ranged from 10 to 100 microns. Based on 600 hours' exposure, only TD Nickel-Chromium exhibited flow reduction at 1400 F; all materials exhibited some flow reduction at 1600 F with Driver-Harris 242 being the best of the four. No material was satisfactory at 1800 F, but TD Nickel-Chromium was the most resistant material at both 1800 and 2000 F.

TITANIUM ALLOYS

The factors which promote the reaction between hydrogen and titanium at room temperature have been investigated at Battelle-Columbus.[10] Reactions occurred only with high-purity hydrogen. At pressures up to 20 psig, hydriding occurred only on material which was vacuum annealed to dissolve the surface oxide film. Above 20 psig, the reaction could be initiated on most surfaces by abrading or galling immediately preceding exposure to hydrogen. The tendency toward reaction with hydrogen was increased by increasing the hydrogen pressure or temperature, oily contamination during galling or abrasion, and an acicular microstructure. Factors which inhibited the reaction were contaminants in the hydrogen, exposure to air after galling or surface abrasion, and pickling in $HF-HNO_3$ solution to remove surface metals.

The phase composition and associated microstructure of alpha and alpha plus beta titanium alloys have been related to stress-corrosion cracking in research conducted at Boeing.[11] Precracked, notched bent beams were exposed to 3.5 percent NaCl solution at room temperature. Only a low-interstitial, commercially pure alpha alloy (Ti-50A) was immune to stress-corrosion cracking. Susceptibility to cracking was promoted by alloying additions of oxygen, aluminum, or aluminum and tin each of which restricted slip in the alpha phase. The formation of ordered domains of $Ti_3(Al,Sn)$ further restricted slip and increased cracking susceptibility. Alloying with molybdenum or vanadium improved stress-corrosion cracking resistance presumably by the stabilization of the ductile beta phase. However, the precipitation of a fine dispersion of alpha or omega in the beta phase reduced the stress-corrosion threshold. The formation of intermetallic compounds in alloys containing silicon or copper also promoted cracking susceptibility.

The mechanism of stress-corrosion cracking of Ti-6Al-4V alloy in methanol is being studied at the Air Force Materials Laboratory.[12,13] Electron diffraction studies of the fracture surface produced by tensile testing at 1.7×10^{-5} sec $^{-1}$ in anhydrous methanol have revealed a hard second phase of TiH_2 associated with the presence of Ti_3Al. The results were interpreted to indicate that the stress-corrosion cracking of Ti-6Al-4V in anhydrous methanol is a form of hydrogen embrittlement that occurs by the presence of Ti_3Al or by ordered regions in the microstructure.

MISCELLANEOUS ALLOY SYSTEMS

The mechanisms of stress-corrosion cracking of titanium alloys and high-strength steels are being investigated at The Ohio State University.[14] Electrochemical, sonic, ellipsometric, hydrogen permeation, field ion emission, and LEED (low energy electron diffraction) techniques were employed. The initiation of cracks in titanium alloys was shown to depend on the state of stress, applied potential, the concentration of salt water in the methanol environment studied, and the rolling direction. Cracking in high-strength steels depended on the pH of the buffered solutions and increased with decreasing pH.

The Air Force Materials Laboratory has evaluated the corrosion behavior of welded and brazed stainless steels and superalloys in hot salt-air environment.[15] Tensile tests were conducted on specimens coated with 0.002 inch of dried simulated sea salt prepared from a solution containing 25 g/l NaCl, 11 g/l $MgCl_2 \cdot 6H_2O$, 4 g/l Na_2SO_4, and 1.2 g/l $CaCl_2$. The specimens were cycled from room temperature to 600 to 800 F (aircraft structures), or 800 to 1200 F (power-plant compressor), or 1600 to 2000 F (power-plant hot section). The results of the study are summarized in Table 1.

The flaw growth characteristics of Alloy 718 and 2219-T6E46 aluminum in pressurized hydrogen have been studied by Boeing.[16] Surface-flawed fracture toughness specimens and preflawed Alloy 718 pressure vessels were exposed to purified hydrogen at 5200 psig and ambient temperature. The Alloy 718 experienced a drastic reduction of sustained load-carrying capability to 15 percent of its basic fracture toughness for the base metal and to 22 percent for weldments. The base metal and weldments of 2219-T6E46 aluminum retained their load-carrying capability in the pressurized hydrogen.

The susceptibility of austenitic stainless steels and nickel-base alloys to hydrogen embrittlement at temperatures between -100 and 200 C (-148 and 392 F) has been studied in Sweden.[17] Unnotched tensile specimens were pulled to fracture after cathodic charging in a molten $KHSO_4$ bath at 280 to 290 C (535 to 555 F). No hydrogen embrittlement occurred in iron-nickel-chromium alloys containing 18 percent chromium and 15 to 35 percent nickel. Alloys with compositions above and below these ranges were embrittled. Maximum susceptibility to embrittlement occurred at -50 C (-58 F). Microcracks observed during deformation in the embrittled alloys formed preferentially in the twin boundaries of the austenite (Fe-18Cr-11Ni and 16Cr-75Ni-7Fe) and also at inclusions and grain boundaries in the 16Cr-75Ni-7Fe alloy.

The effects of high-pressure hydrogen at room temperature on 35 iron-, nickel-, titanium-, aluminum-, and copper-base alloys have been investigated by Rocketdyne, North American Rockwell.[18-20] The following results were reported for tensile tests on notched and unnotched tensile specimens exposed in 10,000 psi hydrogen:

TABLE 1. SUMMARY OF TYPES OF CORROSION FOUND FOR ALLOYS TESTED[15]

Material and Joint		Salt Corrosion[a] Type (1)	Type (2)	Type (3)	Other Corrosion
AM 350	Weld	800 F	--	800 F	--
		--	--	600 F	--
AM 350	Braze	800 F	--	800 F	--
PH15-7Mo	Braze	--	--	--	800 F[b]
		--	--	--	600 F
PH14-8Mo	Braze	--	--	--	800 F[b]
Hastelloy X	Braze	--	2000 F	--	--
		--	1600 F	--	--
René 41	Weld	--	1800 F	--	--
		--	1600 F	--	--
René 41	Braze	1800 F	1800 F	--	1600 F[c]
Udimet 700	Weld	--	--	--	1600 F[d]
Udimet 700	Braze	--	1600 F	--	--
A-286	Weld	--	1200 F	--	--
A-286	Braze	--	1200 F	--	--
TD Nickel	Braze	--	--	--	2000 F[e]

(a) Three types of salt corrosion were observed in test specimens:
Type (1) Evidenced by localized discoloration on the fracture surface, indicating the existence of a crack during exposure of the specimen to elevated temperatures
Type (2) Evidenced by post-exposure, room-temperature, tensile-property degradation
Type (3) Evidenced by unusual cracking during post-exposure, room-temperature tensile testing.
(b) Corrosion indications were found in both salted and unsalted specimens in the areas affected by the brazing process.
(c) Galvanic corrosion was evident on brazed and salted specimens.
(d) Evidence of sulfidation on one specimen.
(e) Salt accelerated deterioration at braze/parent-metal interface.

(1) Negligible embrittlement: aluminum alloys, stable austenitic stainless steels, A-286, and OFHC copper,

(2) Slight embrittlement: Types 304L and 305 stainless steel, beryllium-copper, and commercially pure titanium,

(3) Severe embrittlement: ductile lower strength steels, Armco iron, pure nickel, and titanium-base alloys, and

(4) Extreme embrittlement: high-strength steels and high-strength nickel-base alloys.

Also investigated were the effects of exposure time, hydrogen pressure, notch severity, low-cycle fatigue, surface abrasion, and protective measures and the relationship between the mechanical properties of steel (in air) and susceptibility to embrittlement in the high-pressure hydrogen.

REFERENCES

(1) Salvinski, R. J., Howell, G. W., and Lee, D. H., "Advanced Valve Technology--Volume II. Materials Compatibility and Liquid Propellant Study", Report NASA CR-96639, TRW Systems Group, Redondo Beach, Calif., Contract NAS 7-436 (November 1967).

(2) Lauchner, E. A., "Design and Processing Requirements to Prevent Stress Corrosion in Aluminum Alloys", Norair Division, Northrop Corporation, Hawthorne, Calif., Paper W9-14.4 presented at the 1969 Western Metal and Tool Conference and Exposition, Los Angeles, Calif., March 10-13, 1969.

(3) Mackie, W. L., "Anticorrosion Sealing Caps for Mechanical Fasteners", Technical Memorandum PMR-TM-68-4 (AD 679697) Pacific Missile Range, Point Mugu, Calif. (September 12, 1968).

(4) Kowaka, M., and Nagata, S., "Transgranular Stress-Corrosion Cracking of Mild Steels and Low Alloy Steels in the H_2O-CO-CO_2 System", Corrosion, 24 (12), 427-428 (December 1968).

(5) Smith, J. H., and Rolfe, S. T., "Effect of Composition on the K_{ISCC} of Experimental HY-150 Steels", Report 39.018-016(10), Applied Research Laboratory, U. S. Steel Corporation, Monroeville, Pa., Contract NObs-9535(FBM) (December 20, 1968).

(6) Carter, C. S., "Crack Extension in Several High-Strength Steels Loaded in 3.5% Sodium Chloride Solution", Report D6-19770, Commercial Airplane Division, The Boeing Company, Renton, Wash., Contract N00014-66-C-0365 (November 1967).

(7) Lennox, Jr., T. J., Peterson, M. H., and Groover, R. E., "Marine Corrosion Studies--The Corrosion Characteristics and Response to Cathodic Protection of Several Stainless Steel Alloys in Quiescent Sea Water", NRL Memorandum Report 1948, Naval Research Laboratory, Washington, D. C. (November 1968).

(8) DeClue, D., "Evaluation of Armco PH13-8Mo Martensitic Stainless Steel", Final Report 513-713, McDonnell Company, St. Louis, Mo. (September 17, 1968).

(9) Kaufman, A., "Analytical Study of Flow Reduction Due to Oxidation of Wire-Form Porous Sheet for Transpiration Cooled Turbine Blades", Report NASA TN D-5001, NASA, Lewis Research Center, Cleveland, O. (January 1969).

(10) Koehl, B. G., Williams, D. N., and Bartlett, E. S., "Investigation of the Reaction of Titanium with Hydrogen", Report NASA CR-92389, Battelle Memorial Institute, Columbus, O., Contract NAS 9-7549 (March 18, 1969).

(11) Curtis, R. E., "Relationship Between Composition, Microstructure, and Stress-Corrosion Cracking in Titanium Alloys", Report D6-23716, Commercial Airplane Division, The Boeing Company, Renton, Wash., Contract N00014-66-C-0365 (October 1968).

(12) Gegel, H. L., and Fujishiro, S., "The Mechanism of Stress-Corrosion Cracking of Ti-6Al-4V Alloy in Anhydrous Methanol", Report AFML-TR-68-290, Air Force Materials Laboratory, Wright-Patterson Air Force Base, O. (January 1969).

(13) Gegel, H. L., and Fujishiro, S., "On The Mechanism of Stress-Corrosion Cracking of a Titanium-6% Aluminum-4% Vanadium Alloy in Anhydrous Methanol", Journal of the Less-Common Metals, 17 (3), 305-311 (March 1969).

(14) Fontana, M. G., "Corrosion Cracking of Metallic Materials", Final Report AFML-TR-69-16, The Ohio State University, Columbus, O., Contract AF 33(615)-5108 (February 1969).

(15) O'Conner, J. J., and Vozzella, P. A., "Evaluation of Welded and Brazed Stainless Steels and Superalloys in a Corrosive Environment", Final Report AFML-TR-67-258, Pratt & Whitney Aircraft Division, United Aircraft Corporation, East Hartford, Conn., Contract AF 33(615)-5129 (October 1968).

(16) Lorenz, P. M., "Effect of Pressurized Hydrogen upon Inconel 718 and 2219 Aluminum", The Boeing Company, Seattle, Wash., Paper W9-13.2 presented at the 1969 Western Metal and Tool Conference and Exposition, Los Angeles, Calif., March 10-13, 1969.

(17) Lagneborg, R., "Hydrogen Embrittlement in Austenitic Steels and Nickel-Base Alloys", J. of the Iron and Steel Institute, 207 (3), 363-366 (March 1969).

(18) Walter, R. J., and Chandler, W. T., "Effects of High-Pressure Hydrogen on Metals at Ambient Temperature", Final Report R-7780-1, Rocketdyne Division, North American Rockwell Corporation, Canoga Park, Calif., Contract NAS 8-19 (February 28, 1969).

(19) Walter, R. J., and Chandler, W. T., "Effects of High-Pressure Hydrogen on Metals at Ambient Temperature", Final Report R-7780-2, Rocketdyne Division, North American Rockwell Corporation, Canoga Park, Calif., Contract NAS 8-19 (February 28, 1969).

(20) Walter, R. J., and Chandler, W. T., "Effects of High-Pressure Hydrogen on Metals at Ambient Temperature", Final Report R-7780-3, Rocketdyne Division, North American Rockwell Corporation, Canoga Park, Calif., Contract NAS 8-19 (February 28, 1969).

DMIC Reviews of Recent Developments present brief summaries of information which has become available to DMIC in the preceding period (usually 3 months), in each of several categories. DMIC does not intend that these reviews be made a part of the permanent technical literature. Copies of referenced reports are not available from DMIC; most can be obtained from the Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314.

R. W. Endebrock, Editor